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(54) Title: **PROCESS FOR PREPARING FLEXOGRAPHIC PRINTING PLATES**

(57) Abstract: A process for preparing flexographic printing plates, which process comprises selectively curing a flexographic printing plate precursor made of a photo-curable composition comprising a thermoplastic material, and removing at least part of the thermoplastic material that has not been cured above 60 °C by shear force. The invention also provides a photo-curable composition for use in such a process.

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PROCESS FOR PREPARING FLEXOGRAPHIC PRINTING PLATES

Field of the Invention

The present invention relates to a process for preparing flexographic printing plates. Moreover, it relates to photo-curable polymer compositions of which such printing plates may be made.

Background of the Invention

Flexographic printing plates are well known in the art and are especially useful for commercial printing on diverse products such as flexible plastic containers, cartons, plastic bags, boxes and envelopes.

For the purpose of this specification, uncured plates to be used for preparing (cured) flexographic printing plates are referred to as flexographic printing plate precursors (or "FPP precursors").

FPP precursors typically comprise a layer prepared from a photo-curable polymer composition on the side that is to be used for printing, which may be selectively cured by exposing the photo-curable layer image-wise to light, e.g. UV light. The unexposed (uncured) parts of the layer may then be removed in developer baths, typically with an organic solvent. After drying, the flexographic printing plate is ready for use.

It will be appreciated that the removal of uncured parts (developing) of the flexographic printing plates must be done in a precise manner. Any unintentional uncured residue that is left on the flexographic printing plate may lead to an unclear image on the flexographic printing plate, and, hence unclear prints.

Photo-curable compositions comprising block copolymers containing at least two monovinyl aromatic hydrocarbon polymer blocks separated by at least one

conjugated diene polymer block, are well known to those skilled in the art.

A disadvantage of photo-curable compositions comprising such block copolymers is that the resulting flexographic printing plates typically need to be developed with organic solvent to obtain good results.

Primarily for environmental reasons, uncured portions of the flexographic printing plate may also be removed by water. Water, however, is a bad solvent for (hydrophobic) block copolymer compositions. Therefore, typically hydrophilic polymers are added to the photo-curable composition, the said polymers having a preferred acid or amine value of 20 to 80, as described in EP-A-0 513 493 and WO 00/00546.

United States patent specification No. 5,422,225 describes water-washable printing plates containing a water-dispersible elastomeric polymer blend. The block copolymer contains polymer blocks of an acrylic monomer containing acid groups, in order to make the block copolymer better soluble in water.

Still, both methods have not produced the desired results. It would therefore be desirable if a process could be found for preparing objects of photo-cured polymer compositions, and for developing printing plates in particular, that does not require the use of an organic solvent.

Summary of the Invention

Surprisingly an elegant process has now been found to prepare flexographic printing plates in the absence of an organic solvent. Accordingly, the present invention relates to a process for preparing flexographic printing plates, which process comprises selectively curing a flexographic printing plate precursor made of a photo-curable composition comprising a thermoplastic material,

and removing at least part of the thermoplastic material that has not been cured above 60 °C by shear force.

There is also provided a photo-curable composition of which said flexographic printing plates may be made.

5 Detailed description of the Invention

10 The present invention is based on the property of thermoplastic polymers to be fluid above their softening temperatures. Subsequently, the fluid thermoplastic material may be removed by various methods, for instance by directing a stream of a pressurized gas or fluid onto the object. Alternatively or concurrently, the fluid thermoplastic material may be brushed away.

15 The flexographic printing plate can be heated to the desired temperature by methods known in the art. For instance, it may be heated by suspension in a hot water bath. This is the preferred method.

20 The photo-curable polymer composition comprises a thermoplastic polymer that may be cured in the presence of a photo-initiator, and a photo-initiator capable of curing said thermoplastic polymer. Selection of the thermoplastic polymer and photo-initiator depends on the intended use of the photo-cured object made by the process of the present invention. Of particular suitability are styrenic block copolymers (thermoplastic elastomers typically based on polystyrene blocks and polydiene blocks) as described in Chapter 3 of
25 "Thermoplastic Elastomers, a comprehensive review" (1987), edited by N.R.Legge, G.Holden, H.E.Schroeder, Hanser publishers.

30 The present invention is particularly suitable for the preparation of flexographic printing plates, made of a novel photo-curable composition. This novel composition comprises:

35 (a) from 10 to 37% by weight of one or more block copolymers having at least two blocks A of predominantly

polymerised mono-vinyl aromatic monomer linked by at least one block B of predominantly polymerised conjugated diene monomer, that each or in combination exhibit a tensile strength above 28 MPa as measured by ASTM D-412 and wherein the total weight fraction of the A blocks is between 10 and 35% by weight;

(b) more than 50% by weight of one or more oligomers of structure B or A-B and having a weight average molecular weight in the range from 300 to 100,000 that each or in combination exhibit a tensile strength below 3 MPa as measured by ASTM D-412 and wherein the total weight

fraction of the A blocks is between 0 and 35% by weight;

(c) an ethylenically unsaturated radically polymerisable agent which is at least partially compatible with polymer blocks A in such amount that the total fraction of the A blocks and of (c) is less than 25% but more than 12% by weight; and

(d) from 0.01% to (c)/5% of a photo-initiator (all % by weight relative to the weight of the photo-curable composition).

The above composition may be selectively cured by the process of the present invention, whereupon material that is not cured may be removed at a temperature in the range of 60 °C to 160 °C.

Preferably, component (a) is a linear block copolymer. More preferably, this block copolymer has the structure A-B-A.

The total weight average molecular weight of the block copolymer (a) is preferably in the range of from 50,000 to 300,000 g/mol. More preferably, the weight average molecular weight is in the range from 65,000 to 250,000.

The weight average molecular weight can be determined with gel permeation chromatography (GPC) using

polystyrene calibration standards (according to ASTM D 3536).

From the measured apparent molecular weight (sometimes referred to as peak molecular weight) the (true) weight average molecular weight can be calculated. The apparent molecular weight is the molecular weight as if the polymer is 100% polystyrene as polystyrene calibration standards are used. The weight average molecular weight as used herein is a "true" molecular weight which takes the chemical composition of the polymer into account.

The total poly(mono-vinyl aromatic) content of the first block copolymer is preferably in the range from 10 to 22% by weight, more preferably 15 to 20% by weight.

The composition may comprise a second block copolymer of the structure A-B. The total weight average molecular weight of the second block copolymer, if any, is preferably in the range of more than 35,000 to 150,000. More preferably, the weight average molecular weight is in the range from 40,000 to 150,000, even more preferably in the range from 45,000 to 120,000.

The total poly(mono-vinyl aromatic) content of the second block copolymer is preferably in the range from 5 to 25% by weight, more preferably 10 to 22% by weight, even more preferably 15 to 20% by weight.

The expression "predominantly" used in respect of the monomers of which the block copolymers are made of indicate that up to 20 percent of these monomers may be of a different type.

The mono-vinyl aromatic monomer is typically selected from styrene, C₁-C₄ alkylstyrene and C₁-C₄ dialkylstyrene, in particular styrene, α -methylstyrene, o-methylstyrene or p-methylstyrene, 1,3-dimethylstyrene,

p-tert.-butylstyrene or mixtures thereof, most preferably styrene.

The conjugated diene monomer is typically a conjugated diene monomer containing from 4 to 8 carbon atoms, such as 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, preferably butadiene or isoprene or mixtures thereof, most preferably isoprene.

If 1,3-butadiene is used as the conjugated diene monomer, it may be preferred that a substantial part of the 1,3-butadiene is polymerized via 1,2 addition rather than via 1,4 addition. That is, according to one embodiment the 1,2 vinyl content of the butadiene block is preferably at least 25% by weight, more preferably from 30 to 80% by weight.

The blocks of predominantly polymerised conjugated diene monomer may be (partly) hydrogenated.

Block copolymers are typically prepared by anionic polymerization. The preparation of block copolymers is well known to those skilled in the art and has been described in e.g. US patents 3,265,765; 3,231,635; 3,149,182; 3,238,173; 3,239,478; 3,431,323; Re. 27,145, and many handbooks including "Thermoplastic Elastomers, a comprehensive review" mentioned above.

Photo-initiators are known to those skilled in the art and examples of suitable photo-initiators have been disclosed in European patent specification No. 0 696 761 and US patent Nos. 4,894,315; 4,460,675 and 4,234,676. Typically, the photo-initiator is selected from optionally substituted polynuclear quinones, aromatic ketones, benzoin and benzoin ethers and 2,4,5-triaryl-imidazolyl dimers. Preferred photo-initiators are those described in WO 00/00546.

Preferably, the photo-curable polymer composition comprises 0.01 to (c)/5% by weight of photo-initiator,

basis the total photo-curable polymer composition, preferably 0.1 to (c)/2.5% by weight.

Component (b) is a plasticizer. Plasticizers are well known to those skilled in the art. Typically, the hardness of a printing plate is decreased by adding a plasticizer to the photo-curable polymer composition. The plasticizer is typically compatible with at least the diene blocks of the elastomer.

Examples of plasticizers commonly used include oil and liquid polyolefins such as polyisoprene. Examples of alternative plasticizers which may be used in the composition of the invention are, oligomers of randomly polymerized styrene and conjugated diene, polybutylene, polybutadiene, polybutene-1, and ethylene-propylene-diene rubber, all having a weight average molecular weight in the range from 300 to 35,000, preferably from 300 to 25,000, more preferably from 500 to 10,000.

Alternatively, the plasticizer is a low molecular weight block copolymer having one block A of polymerized mono-vinyl aromatic monomer, and at least one block B of polymerised conjugated diene monomer. The weight average molecular weight of the low molecular weight block copolymer is preferably from 5,000 to 32,000, more preferably from 10,000 to 30,000. The total poly(mono-vinyl aromatic) content of the low molecular weight block copolymer is preferably in the range from 5 to 25% by weight, more preferably from 10 to 22% by weight, even more preferably 12 to 20% by weight.

Most preferably, the plasticiser to be used is polyisoprene.

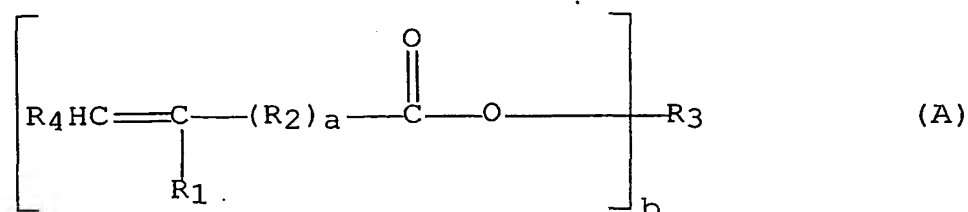
Component (c) is at least partially compatible with the block copolymer(s). Monomers that can be used as component (c) in the novel photo-curable composition of the present invention are well known in the art. Examples

of such monomers can be found in US Patents 4,323,636;
4,753,865; 4,726,877 and 4,894,315.

Typically, the ethylenically unsaturated radically-
polymerisable agent has a boiling point of at least
100 °C at atmospheric pressure and a molecular weight of
up to 3000, preferably up to 2000.

Preferably, this agent is at least partially
compatible with polymer blocks A, and not compatible with
polymer block(s) B. Examples of suitable ethylenically
unsaturated radically-polymerisable agents include esters
of acrylic acid or methacrylic acid, styrene and
derivatives thereof, esters of maleic acid or fumaric
acid, acrylamide or methacrylamide and allyl compounds.

More preferably, component (c) is selected from one
or more compounds containing C₃-C₇ alkenoic acid ester
groups of formula A,



wherein R₁ is hydrogen or a C₁-C₄ alkyl group; R₂ is a
C₁-C₃ alkane group; R₃ is a C₁-C₈ arene, alkane or
cycloalkane group; R₄ is hydrogen or a methyl group; a is
0 or 1; and b is an integer in the range from 1 to 6.

According to a particularly preferred embodiment the
compound containing C₃-C₇ alkenoic acid ester groups is
selected from those compounds represented by formula A in
which a is 0 and b is an integer in the range from 1 to
4. Most preferably, esters of acrylic acid or methacrylic
acid are used. Especially preferred monomers are
1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate,
and hydroxyethyl methacrylate.

For the purposes of this specification, the compatibility between two ingredients can be assessed via the transparency and macroscopic homogeneity of a mixture of the two considered ingredients at their weight ratio used in the formulation and at room temperature. Such mixture is said to be compatible if transparent and without any bleeding out or macroscopic separation of one ingredient from the mixture. At the opposite, two ingredients are said to be incompatible if the said mixture exhibits a non-transparent (i.e. milky) appearance and/or if at least one ingredient has a macroscopically evident tendency to bleed out of the mixture. This compatibility concept has been described in US patent specification No. 3,917,607, incorporated herein by reference.

The photocurable composition may further comprise one or more stabilisers such as antioxidants, UV stabilisers and radical scavengers, as well as any other additives known to those skilled in the art to be desirable in photo-curable compositions.

Stabilisers such as antioxidants/UV stabilisers/radical scavengers are also well known to those skilled in the art.

Especially hindered phenols, organo-metallic compounds, aromatic amines, aromatic phosphites and sulphur compounds are useful for this purpose. Preferred stabilisers include phenolic antioxidants, thio compounds and tris(alkyl-phenyl) phosphites.

The stabiliser(s) is (are) typically present in the photo-curable composition in a total amount from 0.01 to 5% by weight, basis the total photo-curable composition, preferably 0.2 to 3% by weight.

Other well known components that may be present in the photo-curable polymeric composition include polymerisation inhibitors, antiozonants, colorants,

fillers or reinforcing agents. It belongs to the skill of the skilled person to select the appropriate additional components in the appropriate amounts.

5 Cross-linking is typically carried out by subjecting the photo-curable composition to actinic radiation as described in WO 00/00546.

10 Most flexographic printing plates are uniformly post-exposed to ensure that the photocross-linking process is complete, and optionally subjected to a detackification treatment according to procedures known to those skilled in the art as e.g. described in EP-A-0 474 178.

15 The process as described herein is especially suitable for developing printing plates. Accordingly, the present invention further relates to a process for preparing a flexographic printing plate which comprises cross-linking part of a cross-linkable printing plate precursor with actinic radiation to prepare a partially cross-linked printing plate precursor; removing not-cross-linked material from the partially cross-linked printing plate precursor by a process as outlined above;
20 and, optionally, drying to obtain the printing plate.

C L A I M S

1. A process for preparing flexographic printing plates, which process comprises selectively curing a flexographic printing plate precursor made of a photo-curable composition comprising a thermoplastic material, and removing at least part of the thermoplastic material that has not been cured above 60 °C by shear force.
2. A process as claimed in claim 1, wherein the shear force is applied by directing a stream of a pressurized gas or fluid onto the object, and/or by brushing the thermoplastic material away.
3. A process as claimed in any one of the preceding claims, wherein the object is heated by suspension thereof in a hot water bath.
4. A process as claimed in any one of the preceding claims, wherein the photo-curable composition is cured by exposure to actinic radiation.
5. A process as claimed in any one of the preceding claims, wherein the photo-curable composition comprises:
 - (a) from 10 to 37% by weight of one or more block copolymers having at least two blocks A of predominantly polymerised mono-vinyl aromatic monomer linked by at least one block B of predominantly polymerised conjugated diene monomer, that each or in combination exhibit a tensile strength above 28 MPa as measured by ASTM D-412 and wherein the total weight fraction of the A blocks is between 10 and 35% by weight;
 - (b) more than 50% by weight of one or more oligomers of structure B or A-B and having a weight average molecular weight in the range from 300 to 100,000 that each or in combination exhibit a tensile strength below 3 MPa as

measured by ASTM D-412 and wherein the total weight fraction of the A blocks is between 0 and 35% by weight; (c) an ethylenically unsaturated radically polymerisable agent which is at least partially compatible with polymer blocks A in such amount that the total fraction of the A blocks and of (c) is less than 25% but more than 12% by weight; and

(d) from 0.01% to (c)/5% of a photo-initiator (all % by weight relative to the weight of the photo-curable composition).

6. A photo-curable composition for use in a process as claimed in any one of the preceding claims, which comprises:

(a) from 10 to 37% by weight of one or more block copolymers having at least two blocks A of predominantly polymerised mono-vinyl aromatic monomer linked by at least one block B of predominantly polymerised conjugated diene monomer, that each or in combination exhibit a tensile strength above 28 MPa as measured by ASTM D-412 and wherein the total weight fraction of the A blocks is between 10 and 35% by weight;

(b) more than 50% by weight of one or more oligomers of structure B or A-B and having a weight average molecular weight in the range from 300 to 100,000 that each or in combination exhibit a tensile strength below 3 MPa as measured by ASTM D-412 and wherein the total weight fraction of the A blocks is between 0 and 35% by weight;

(c) an ethylenically unsaturated radically polymerisable agent which is at least partially compatible with polymer blocks A in such amount that the total fraction of the A blocks and of (c) is less than 25% but more than 12% by weight; and

(d) from 0.01% to (c)/5% of a photo-initiator (all % by weight relative to the weight of the photo-curable composition).

7. A composition as claimed in claim 6, wherein component (a) is a linear block copolymer.

8. A composition as claimed in claim 6, wherein component (a) is a linear block copolymer of structure A-B-A.

9. A composition as claimed in claim 6 or 7, wherein component (a) has a weight average molecular weight in the range of from 50,000 to 300,000 g/mole.

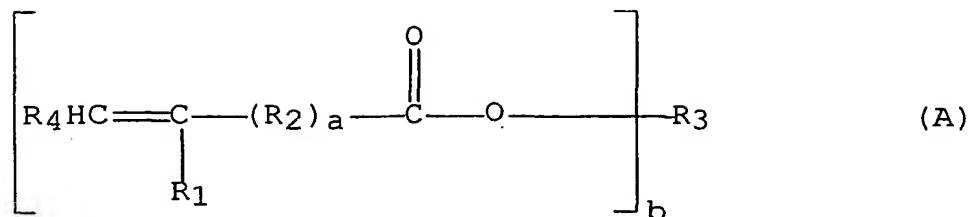
10. A composition as claimed in any one of claims 6 to 9, wherein the mono-vinyl aromatic monomer is selected from styrene, C₁-C₄ alkylstyrene and C₁-C₄ dialkylstyrene, in particular styrene, α -methylstyrene, o-methylstyrene or p-methylstyrene, 1,3-dimethylstyrene, p-tert.-butylstyrene or mixtures thereof, most preferably styrene.

11. A composition as claimed in any one of claims 6 to 10, wherein the conjugated diene monomer is a conjugated diene monomer containing from 4 to 8 carbon atoms, preferably selected from 1,3-butadiene, 2-methyl-1,3-butadiene (isoprene), 2,3-dimethyl-1,3-butadiene, more preferably butadiene or isoprene or mixtures thereof, most preferably isoprene.

12. A composition as claimed in any one of claims 6 to 11, wherein component (b) is a polyisoprene.

13. A composition as claimed in any one of claims 6 to 12, wherein component (d) is selected from optionally substituted polynuclear quinones, aromatic ketones, benzoin and benzoin ethers and 2,4,5-triarylimidazolyl dimers.

14. A composition as claimed in any one of claims 6 to 13, wherein component (c) is a C₃-C₇ alkenoic acid ester groups containing compound of formula A,



wherein R_1 is hydrogen or a C_1 - C_4 alkyl group; R_2 is a C_1 - C_3 alkane group; R_3 is a C_1 - C_8 arene, alkane or cycloalkane group; R_4 is hydrogen or a methyl group; a is 0 or 1; and b is an integer in the range from 1 to 6.

- 5 15. A composition as claimed in claim 14, wherein the compound containing C_3 - C_7 alkenoic acid ester groups is selected from those compounds represented by formula A in which a is 0 and b is an integer in the range from 1 to 4, and where the calculated Small solubility parameter is
- 10 in the range of 8.75 to 9.5 $(\text{cal}/\text{cm}^3)^{1/2}$.

INTERNATIONAL SEARCH REPORT

Int'l Application No

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A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 G03F7/033 G03F7/038 G03F7/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 00 00546 A (SHELL INT RESEARCH) 6 January 2000 (2000-01-06) cited in the application examples	6
A	EP 0 513 493 A (NIPPON PAINT CO LTD) 19 November 1992 (1992-11-19) cited in the application examples	6
A	EP 0 474 178 A (DU PONT) 11 March 1992 (1992-03-11) cited in the application examples	6

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/06057

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0000546	A	06-01-2000	AU 5409099 A BR 9911536 A CN 1307614 T WO 0000546 A1 EP 1091998 A1	17-01-2000 20-03-2001 08-08-2001 06-01-2000 18-04-2001
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